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THE REVERSIBILITY OF THE REACTION OF ALKALI METALS WITH LIQUID AMMONIA

Ernest J. Kirschke

(Ph.D. Thesis)

September 1966

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THE REVERSIBILITY OF THE REACTION OF ALKALI METALS WITH LIQUID AMMONIA

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September 1966

ABSTRACT

Ammoniated electrons exist in solutions of the alkali metal amides in liquid ammonia which have reached thermodynamic equilibrium with hydrogen gas. By using both electron paramagnetic resonance and optical spectroscopy to measure the electron concentration an equilibrium constant of 5×10^4 was measured for the reaction

$$e^-_{am} + NH_3 = NH_2^- + \frac{1}{2} H_2$$

and 3×10^9 for the reaction

$$Na^+ + e^-_{am} + NH_3 = NaNH_{2(c)} + \frac{1}{2} H_2$$

at 25°. By determining the temperature dependence of the electron concentration in these solutions a heat of solution of -19 kcal was estimated for the first reaction and -12 kcal for the second.

I. INTRODUCTION

Solutions of alkali metals in liquid ammonia are metastable and can, particularly in the presence of a catalyst, decompose to form the metal amide and hydrogen according to the reaction:

$$e^-_{am} + NH_3 = NH_2^- + \frac{1}{2} H_2 \qquad (1)$$

if the metal amide remains in solution, or

$$M^+ + e^-_{am} + NH_3 = MNH_{2(s)} + \frac{1}{2} H_2 \qquad (2)$$

if solid metal amide is formed. These reactions are useful in the preparation of amides but often they are undesirable side reactions in the study and use of metal ammonia solutions. Kraus[1] suggested that a systematic study of these reactions was a necessary prelude to the study of more stable solutions. No one has actually measured the thermodynamics of either reaction but Jolly,[2,3] by correlating thermodynamic data for electrolytes in liquid ammonia[4,5,6,7] estimated a value of approximately 10^6 for the equilibrium constant of (1) at 25° and proposed that a solution 1M in NH_2^- in equilibrium with hydrogen at 100 atmospheres pressure would contain 10^{-5} M e^-_{am}. Using the same data, reaction (1) was determined to be exothermic with ΔH° = - 12 kcal. The purpose of this work was to experimentally verify the reversibility of these reactions and to measure directly their equilibrium constants and temperature dependence.

The effect of hydrogen pressure on the electron concentration was measured up to approximately 100 atmospheres in solutions of $NaNH_2$, KNH_2 and $CsNH_2$. The amide ion concentration dependence of this equilibrium was studied primarily in solutions of KNH_2 with two runs in solutions of $CsNH_2$.

The temperature dependence of the equilibrium reaction (1) was investigated for several solutions of KNH_2. A saturated $NaNH_2$ solution was used for studying the temperature dependence of reaction (2). We did not study $NaNH_2$ solutions at concentrations below saturation because the low solubility of $NaNH_2$ (0.17 g/100 g NH_3 at 25°)[8] made them too difficult to prepare in our apparatus. $LiNH_2$ and the amides of the alkaline earths are nearly insoluble and samples containing them failed show an EPR spectrum even when run at temperatures as high as 80° and at hydrogen pressures of 40 atmospheres.

Measurements were made at 25° rather than at the sub zero temperatures normally used in liquid ammonia studies so that the data could be easily compared with other tabulated thermodynamic data. Also, equilibrium is reached more rapidly at the higher temperature, and based on the predicted exothermicity of the reaction, the electron concentration would be much greater at 25° than at 0° or lower.

The basic experimental problem was to measure the concentration of ammoniacal electron at various concentrations of amide and at different hydrogen pressures. The electron in liquid ammonia has a single, extremely sharp paramagnetic resonance absorption (half width ~ 0.06 gauss).[9] This makes it possible to use Electron Paramagnetic Resonance (EPR) to observe very low concentrations of the electron in solution. We found that when measured amounts of potassium and ammonia were sealed in glass tubes and the reaction was allowed to take place, an EPR spectrum corresponding to the parameters measured by Hutchinson and Pastor[9] was observed. The EPR method was employed in several experiments, particularly in the temperature dependence study.

Metal ammonia solutions of even low concentration are intensely blue, indicating a very high extinction coefficient in the near infra red. Gold and Jolly[10] and others[11,12] have studied these solutions at various temperatures and have found the molar extinction coefficient at the absorption peak to be about 10^4 liter moles^{-1}cm^{-1}. Corset and Lepoutre[12,13] made their measurements at 24°, and we used their extinction coefficient data in our calculations. From the equilibrium value estimated by Jolly, we calculated at a 1 molar solution of KNH_2 at 100 atmospheres of hydrogen pressure in a cell with a 10 mm path length would have an absorbance of 0.1. Our early work with EPR indicated that the equilibrium constant was close to 10^5 and this would yield an absorbance of 1. This method was therefore quite suitable for this study and a cell was designed to withstand the high hydrogen pressure required.

II. OPTICAL DETERMINATION OF THE ELECTRON CONCENTRATION

A. Description of the Optical Cell

The high pressure optical cell is shown in Figs. 1 and 2. The body of the cell was made from a heavy piece of stainless steel for three reasons: to resist attack by the solutions to be studied, to contain the high pressures anticipated and to act as an efficient heat reservoir to dissipate the heat absorbed from the IR source by the sample. The windows were made of Pyrex and were approximately 1 cm thick. The O-rings were a special ethylene-propylene composition (Porter Seal Co.) selected for their resistance to attack by metal ammonia solutions. A stainless steel bellows seal valve was used as a master valve for the same reason. Stainless steel, V seated, packed valves were used in the manifold. Stainless steel tubing and Swagelock fittings were used in the construction of the manifold and gage connections. When assembled, the unit could hold 136 atm of helium gas for a period in excess of 24 hours.

Temperature control was accomplished by circulating water from a thermostat through copper heat exchange coils soldered to the body of the cell. The temperature was measured with a Rubicon potentiometer using a copper-constantan thermocouple located in a well a few millimeters from the sample cavity. The temperature was maintained to within ± 0.1°C.

Pressure was determined by means of a stainless steel Bourdon gage with a range of 0 - 2000 psig (136 atm) divided in increments of 20 psig (1.36 atm). By fitting the tip of the gage pointer with a thin piece of flat metal mounted perpendicular to the gage face, readings could be estimated at ±1/10 of a division (±0.14 atm).

The cell was mounted on a base plate with adjustable clamps designed to permit accurate, reproducible positioning of the unit in the sample

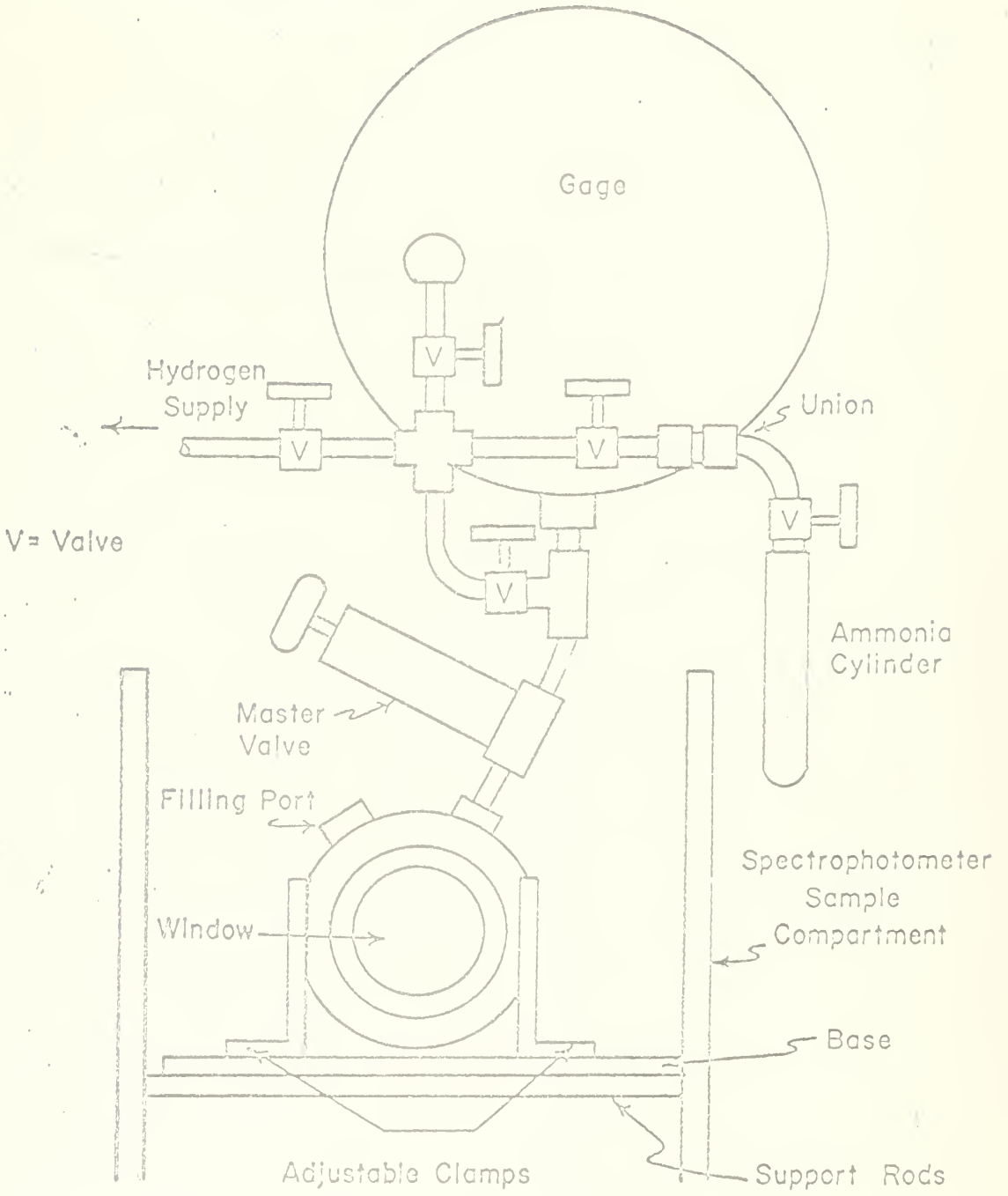

Fig. 1 Optical Cell Viewed Along Axis of the Light Beam.

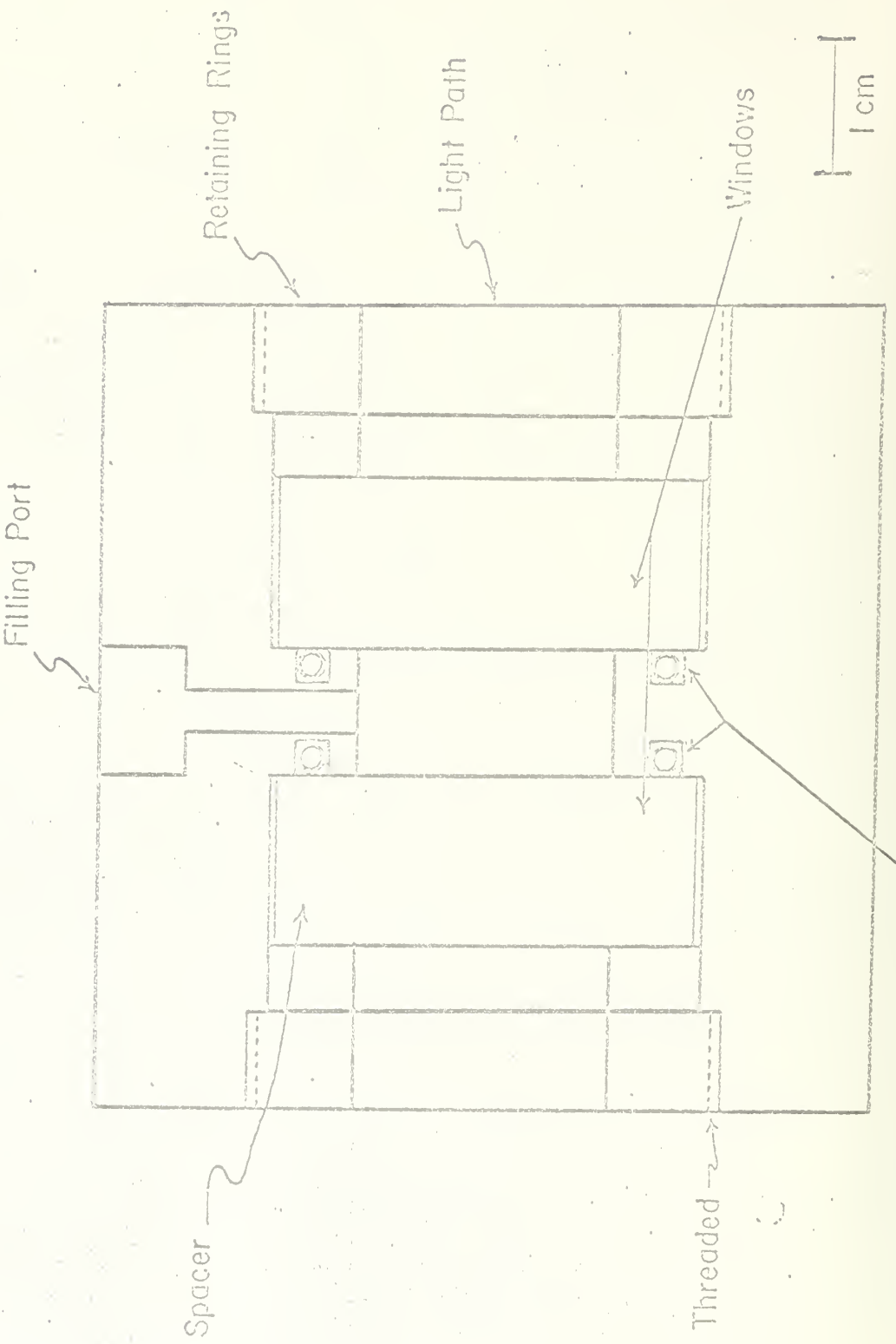

Fig. 2 Cross Section of Optical Cell Through Filling Port.

compartment of a Cary model 14 recording spectrophotometer. Once the proper position had been established, the cell could be repositioned by simply ensuring that two edges of the base plate were in firm contact with two walls of the compartment.

B. Calibration of the Optical Cell

The light path length of the optical cell was mechanically measured with a micrometer caliper. First, the thickness of the metal at the sample cavity was measured to determine the path length, then, after carefully measuring the thickness of the glass windows, the cell was assembled and the retaining ring tightened. The distance between the outer faces of the glass windows was measured. The thickness of the glass was subtracted to give the path length. The two measurements agreed within the accuracy of the instrument indicating that there was glass to metal contact and the O-ring does not effect the path length. The cell was pressurized and the path length measured again. The procedure was repeated at several pressures. The results are listed in Table I.

The light path length was also checked against a cell of known path length using the 12000 A absorption band of a solution of methanol in ethyl ether. A value of 9.96 mm was obtained which, considering the possible errors in this technique, agrees with the mechanical measurement. The values listed in Table I were used in our calculations.

The cell was filled with liquid NH_3 and the effect of pressure on the spectrum was checked at several pressures up to about 130 atmospheres. Hydrogen gas was used to pressurize the cell. The results indicated an increase in absorbance with pressure. At 100 atmospheres this increase was 1.7%, which was larger than predicted from the path

Table I

Effect of Pressure on the Light Path Length of the Optical Cell

Gage Pressure atm.	Measured Path length cm ± 0.001	Percent Change
0	0.992	0
10	0.994	0.2
20	0.995	0.3
35	0.998	0.6
70	1.002	1.0
100	1.004	1.2
150	1.006	1.4

length data of Table I. Maybury and Coulter[14] measured the adiabatic compressibilities of liquid ammonia solutions and from this data we estimated an increase in the density of liquid ammonia of 0.5% per 100 atmospheres increase in pressure. We conclude that the measured increase in the absorption was the result of a change in both path length and density.

When calculating the concentration of the absorbing species from the absorbance data, the net absorbance was corrected for the density change by multiplying by the factor $(1 - 5 \times 10^{-5} P_{H_2})$. Except at pressures near 100 atmospheres, this correction was negligible. The actual path length at a given pressure, as determined by interpolation of the data in Table I, was used in the Beer-Lambert equation to calculate the electron concentration.

The volume of the cell was checked on a vacuum line by filling the cell to a known pressure of nitrogen, as read on a mercury monometer, and

then Toepler pumping the nitrogen into a gas buret of known volume. The volume of the gage and the manifold were determined in the same manner.

The Bourdon gage was calibrated on a dead weight tester and a calibration chart prepared. Above 10 atmospheres the gage read 0.1 atm high. All readings were corrected by the use of the calibration chart. Periodically we checked the gage against a second calibrated gage and verified the calibration chart. The calibration did not change over the period the gage was in use.

C. Procedure for Obtaining Optical Data

Prior to use, the optical cell was carefully cleaned, the metal surfaces of the sample compartment coated with a solution of 0.05 M chloroplatinic acid and the whole unit dried in an oven at 120°. This procedure left a thin coating of platinum in the cell to act as a catalyst. We prepared the amides in the cell by reacting an alkali metal with liquid ammonia, and without this catalyst the dense blue color of the metal solution persisted for up to several hours. The cell was assembled and leak tested with helium at 136 atm.

The cell was attached to a vacuum line and evacuated. The entire system was wrapped with heating tape and the temperature raised to about 100°. Care was taken to loosen the retaining rings during the bake out to prevent cracking of the windows due to the different coefficient of expansion of steel and pyrex. The cell was pumped out for a minimum of 8 hours and then filled with dry, oxygen free nitrogen or argon. Liquid ammonia was dried on a vacuum line by distilling anhydrous ammonia into an evacuated tube containing sodium metal. The dry ammonia was then distilled into a small steel cylinder (10 ml) equipped with a valve. This valve was closed, the cylinder was removed from the vacuum line and

attached to the manifold of the optical cell. A small hole (1 cm diameter) was cut in the end of a plastic glove bag (I^2R Company, Cheltenham, Penn.) and this was fitted over the filling port of the cell and sealed in place with "Duxseal" plastic sealing compound (Johns-Manville). The bag was continuously flushed with nitrogen or argon which had been passed through a column packed with BTS Catalyst (BASF Colors and Chemicals Inc.) to remove traces of oxygen and then through a column of magnesium perchlorate to remove traces of water. The filling port was opened and a known amount of metal introduced, the port was closed and the cell was evacuated. The valve to the vacuum line was closed, cold water circulated through the cell heat exchanger, and ammonia distilled into the cell. When the cell appeared full, the master valve was closed and ammonia in the manifold condensed back into the steel cylinder using liquid nitrogen. The manifold was again opened to the vacuum line and pressure measured with a thermocouple gage to ensure that no ammonia was left in the manifold. The cylinder was removed and weighed. This proved to be a very simple and accurate method of determining the amount of ammonia used.

In the optical range in which the electron absorption band occurs, ammonia has intense absorption bands. It was necessary to take readings at wave lengths at which the ammonia absorption is a minimum. The total absorbance, A_T, at a given wave length was considered to be the sum of the absorbance of the electron, the ammonia, the amide ion and the glass windows. At zero hydrogen pressure the concentration of the electron is zero. Therefore, the absorbance due to the electron was taken to be the difference in the total absorbance at pressure $P > 0$ and that at $P = 0$.

$$A_{e^-} = A_T(P > 0) - A_T(P = 0)$$

In earlier experiments in order to determine the absorbance at zero hydrogen pressure, the hydrogen produced by the reaction was removed. Amide was prepared in the cell by reacting a metal with ammonia. After all of the blue color had disappeared, the hydrogen and ammonia were carefully removed and the system evaporated to dryness on a vacuum line. A known amount of ammonia was distilled back into the cell as described earlier. Once the hydrogen pressure dependence of the reaction had been thoroughly established, this step was eliminated. Instead, the total absorbance was plotted against the square root of the hydrogen pressure and the line extrapolated to zero hydrogen pressure.

Water at 25° was circulated through the heat exchanger and the system allowed to come to equilibrium. This usually took 1 to 2 hours depending upon the concentration of the amide.

The cell was then positioned in the sample compartment of a Cary model 14 spectrophotometer and the absorbance measured. Because of the sensitivity of the absorption band and the equilibrium to temperature, the sample was exposed to the light source for only short periods, less than 5 seconds and allowed time to dissipate any heat absorbed before taking the next reading. To ensure that equilibrium had been reached, the procedure was repeated at 20 minute intervals until three successive readings gave the same value.

At this point hydrogen gas at approximately 150 atm was added to the manifold. This in turn was carefully bled into the gage section until a pressure near that desired was registered on the gage. The valve to the manifold was closed; the master valve was opened, and the pressure was allowed to equilibrate. This normally took 5 to 10 minutes.

The master valve was then closed and the system allowed to reach chemical equilibrium as established by three successive absorbance readings. This took from one to three hours depending on the concentration of the amide and the pressure used. This procedure was repeated until the desired data had been obtained. To test for reversibility in several runs, the process was reversed, that is hydrogen was removed from the system. It was impossible in this step to prevent some ammonia from coming off with the hydrogen, and, with the exception of saturated solutions, changing the amide concentration. The ammonia coming off was collected by passing the gas being removed very slowly through two traps at liquid nitrogen temperature. The hydrogen was pumped away and the amount of ammonia check by either condensing into a gas bulb and weighing, or absorbing in a known quantity of acid and titrating. Both methods gave the same accuracy. The amide concentration was corrected accordingly.

Throughout the procedure, extreme care had to be taken to prevent liquid ammonia condensing past the master valve and into the gage, resulting in a change in the amide concentration. This was done by both heating the gage to a temperature about 5 degrees greater than the cell and by keeping the master valve closed except when taking a pressure reading.

D. Determination of the Amide Concentration in the Optical Studies

The concentrations of the solutions in the optical cell were determine from the weights of the materials used. The sodium and potassium samples were prepared in a dry bag flushed with dry, oxygen-free argon or nitrogen. A piece of metal was cleaned of all oxide and placed in an extrusion press. A length of wire was extruded and placed into a small weighing bottle which had been baked in an oven at 200° and then cooled in the dry

gas atmosphere. The sample was weighed and placed immediately into the cell. The weighing bottle was then reweighed. When properly handled the metals remained shiny for up to 10 minutes.

Handling cesium presented a much more difficult problem because of its semiliquid state and extreme reactivity. We found that we could deliver accurate volumes of clean cesium into the cell with a micro pipette heated to 30°. The density of cesium at this temperature was estimated at 1.84 g/cc. The metal at 30° was drawn up into the pipette which was kept at the same temperature. The tip of the pipette was then placed into the filling port and dry nitrogen was used to force the metal from the pipette into the cell. If the pipette had been properly cleaned and dried, no reaction occurred and the pipette emptied cleanly. The entire operation took place in a well flushed glove bag.

The volume of the ammonia solution was determined from the weight of ammonia used corrected for the amount of ammonia in the gas phase. Three approximations were necessary in this calculation: first, that the vapor pressure of the solution could be estimated using Raoult's Law: second, that knowing the pressure and volume of the ammonia gas the number of moles of gas could be calculated using van der Waal's equation for which the constants for ammonia are available;[15] third, that the effect of the amide concentration on the volume of the solution could be estimated by adding the volume of the amide formed, calculated from the density of the solid amide,[16] to the volume of the liquid ammonia calculated from its weight and density.[17] By successive approximations the amount of ammonia in the gas phase was calculated and the volume of the liquid determined. Appendix A shows a sample calculation.

III. DETERMINATION OF THE ELECTRON CONCENTRATION BY EPR

A. Preparation of the EPR Samples

The EPR samples were prepared by sealing measured amounts of alkali metal and ammonia in pyrex glass tubes and allowing reaction (1) or (2) to reach equilibrium. In all of the samples studied the intense blue color of the metal solutions had completely faded and was replaced by the yellow color of the amide ion.

The EPR sample tubes consisted of 3-millimeter pyrex tubing which ha been selected for uniformity of wall thickness and bore. The tubes were fitted with a pyrex O-ring joint and annealed. The cross section of each tube was determined gravimetrically using mercury. They were thoroughly cleaned, rinsed with a 0.001 M solution of chloroplatinic acid, and place in an oven at 200° for 2 hours. This left a very fine coating of platinu on the walls to act as a catalyst in the preparation of the amide from th metal and liquid ammonia. The presence of the catalyst did not interfere with the spectrum and without it the reaction to form the amide was extremely slow.

The tubes to be used in a particular experiment were placed on the vacuum line, evacuated and flamed out. They were then filled with dry nitrogen, removed, capped and weighed. The tubes were transferred to a dry bag and charged with samples of the metal which had been extruded from a hand press. The tubes were carefully reweighed, placed back on the vacuum line and evacuated. Dry liquid ammonia was then distilled onto the sample. Based on the weight of metal used and the cross section of the tube, the approximate level of ammonia to give a desired concentration could be determined. The tubes were sealed off and both sections weighed to determine the weight of ammonia used. The tubes were set aside and allowed to react.

Certain experiments called for the addition of sodium bromide, potassium bromide, or both salts to the solution. The salt was dried for several hours at 180° and allowed to cool in a desiccator. Short lengths, 2-3 cm., of melting point capillary, were weighed on a micro balance, filled with an estimated amount of the desired salt and reweighed. The capillary with the salt was placed in the EPR sample tube and the whole unit evacuated and carefully flamed. The sample tubes were filled with dry gas and the samples prepared as described above.

B. Method for Determining the EPR Spectrum

After the reaction had reached equilibrium, usually a few days after the blue color of the metal solution had disappeared, the spectrum was recorded on a Varian V-4502 EPR spectrometer. A small crystal of diphenylpicrylhydrazyl, DPPH, was placed in the cavity near the sample to act as a reference and intermediate standard. The temperature was controlled to ± 0.1° by passing dry air through a heat exchanger and then through a small dewar in which the sample was positioned. Figure 3 shows the arrangement. The temperature could be varied by changing the temperature of the heat exchanger bath and controlling the flow of air. Temperature was measured with a Rubicon potentiometer and copper-constantan thermocouple.

The electron concentration was determined by indirectly comparing the sample signal with that of a solution of recrystallized vanadium (IV) oxyacetylacetonate of known concentration.

The Q value of the microwave cavity is seriously affected by the introduction of samples of varying dielectric strength. A lowering of the Q value decreases the sensitivity of the spectrometer and results in a reduced signal intensity. This was compensated for by means of the DPPH intermediate standard. When the spectrum of each sample and

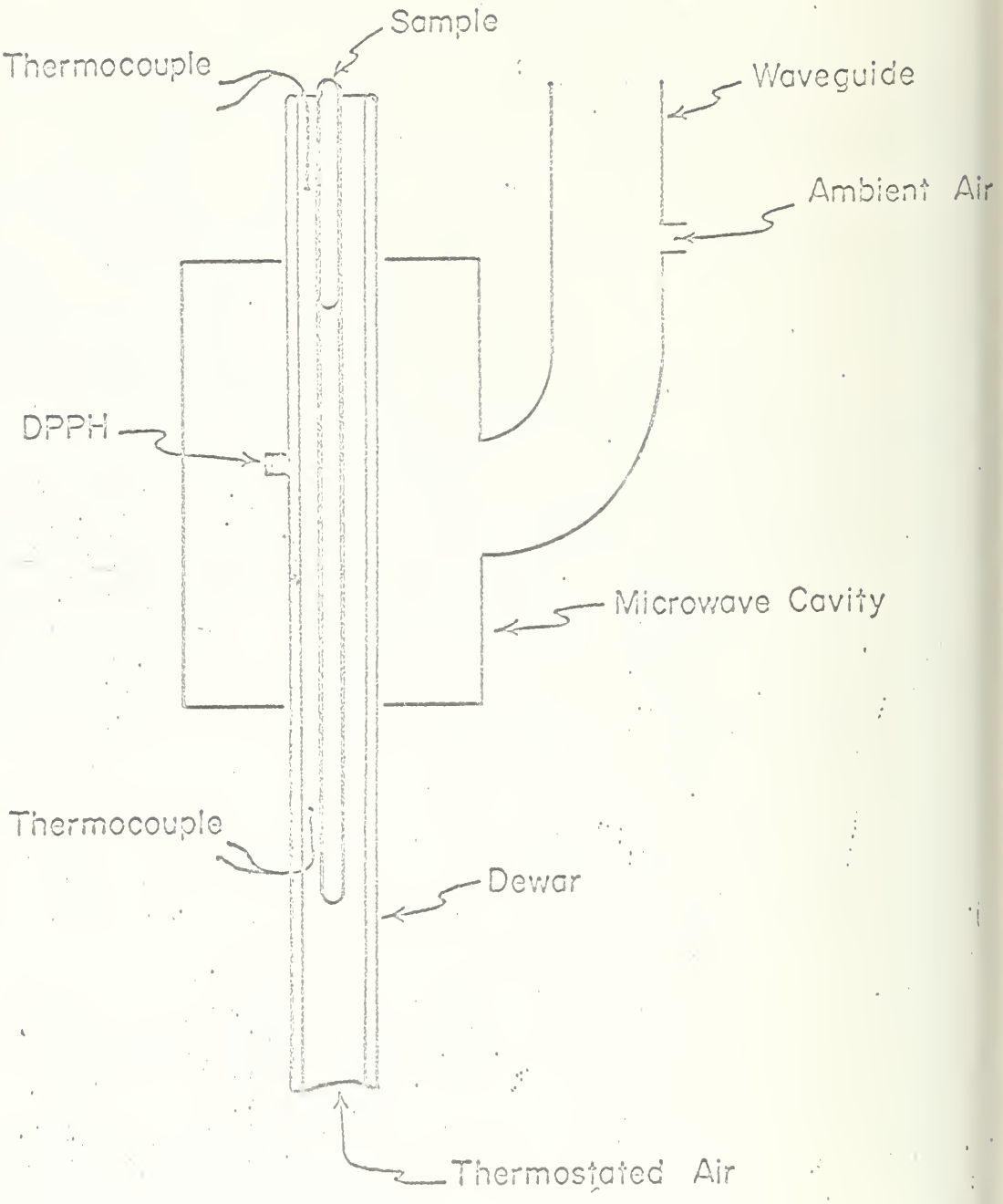

Fig. 3 Schematic of the EPR Microwave Cavity Showing the Arrangement of the Sample and the DPPH Intermediate Reference Standard.

the standard sample was recorded, the spectrum of the DPPH was also recorded. One of the samples was selected as a reference and the ratio of its signal intensity to the signal intensity of each of the other samples was corrected by the ratio of the corresponding DPPH signal intensities according to the equation:

$$\frac{I}{I_R} = \frac{I_{(OBS)}/D}{I_{R(OBS)}/D_R}$$

Then by determining the concentration of spins in the reference sample, the concentration of all of the samples could be calcuated. Details of this calculation are shown in Appendix C.. This technique also accounts for any change in cavity match or r-f power level.[18]

When comparing the relative signal intensities of a series of samples, the instrument was tuned carefully to one sample and all of the settings noted. When the next sample was substituted in the cavity, the fine tuning and leakage current settings usually changed slightly and had to be adjusted to their previous values. The only other adjustment made was in the gain, if necessary, to give a signal of sufficient intensity to be accurately recorded. A number of successive runs were made and the results compared. Readings on a given sample could be duplicated to an accuracy of ± 10%.

The temperature dependence studies were done with the sample left in place in the spectrometer. The temperature was changed and equilibrium allowed to take place. The spectrum was taken at 10 minute intervals and equilibrium was considered to have been reached when 3 successive readings were of the same intensity. The temperature was changed slightly in a direction opposite to the direction in which equilibrium had been shifted and the change in intensity noted. A signal change in the direction predicted by this temperature change indicated we had been at equilibrium.

C. Determination of the Hydrogen Pressure and Amide Concentration of the EPR Sample

The total volume of the prepared sample tube was determined from its internal length and cross section. An adjustment (~ 0.2%) was made for the rounded ends. The volume of liquid was determined by either directly measuring the height in the tube or from the weight and density of the solution. When possible, both methods were used and they agreed within 2%.

After the spectrum had been recorded, the sample tube was placed in a specially built glass vessel which consisted of two lengths of 10 mm pyrex tubing joined by a 29/40 standard tapered joint. The center line of the tubing was eccentric to the center line of the joint. One of the tubes was approximately 20 cm long and had a sealed end. This held the sample tube. The other tube was 10 cm long and had been fitted with a vacuum stop cock and a ball joint. The vessel was attached to a vacuum line and evacuated. The tube was filled with dry nitrogen gas and then the long end was placed in liquid nitrogen to freeze the sample. The vessel was again evacuated and removed from the line. With the center line of both tubes in line, the vessel was inverted allowing the sample to slide part way into the short tube. The sample tube was broken by simply rotating the unit about the axis of the joint to put the center-lines of the tubes out of alignment. By means of a Toepler pump, the hydrogen was pumped into a gas buret and measured. Two liquid nitrogen traps in series were used to prevent ammonia from reaching the buret. The vessel containing the broken sample tube was warmed very slowly from liquid nitorgen temperature to prevent sudden surges of ammonia through the system. A thermocouple vacuum gage was used to determine when all

of the hydrogen had been transferred to the buret.

This measurement determined the total amount of hydrogen produced in the reaction. Using the solubility data of Weibe and Tremaerne[19] and the volume data we determined the pressure of hydrogen in the tube. For every $\frac{1}{2}$ mole of hydrogen formed, one mole of amide forms according to the reaction

$$M + NH_3 = MNH_2 + \frac{1}{2} H_2$$

and from the total hydrogen produced we can also calculate the amide concentration. See Appendix B.

IV. RESULTS OF THE OPTICAL STUDY

The optical spectra of solutions of $NaNH_2$, KNH_2 and $CsNH_2$ were recorded at 13,650 A and at hydrogen pressures up to approximately 100 atmospheres. The results are shown in Table II. As previously stated, readings had to be taken at a wave length where the ammonia absorbance exhibits a minimum. It was desirable that this minimum be fairly broad (about 500 A) and at a wavelength for which the value of the extinction coefficient of the electron spectrum was as high as possible. We found that the minimum at 13,650 A satisfied both of these conditions and gave the most reproducible results. As a comparison, some measurements were made at 11,200; 12,500; 16,000 and 17,500 A, but gave less aeeeptable results.

The electron concentration at a hydrogen pressure P was calculated as follows: From the value of the total absorbanee at pressure P we subtraeted the absorbance at P = 0 and multiplied the difference by the density correetion, to give the net absorbance due to the electron. The concentration of the cleetron was ealculated by substituting the values of the net absorbanee A_{e^-}, the extinction coeffieient ϵ, and the path length d (Table I) into the Beer-Lambert equation.

$$[e^-] = A_{e^-}/\epsilon d$$

For example, the net absorbanee of the 2.01 M KNH_2 solution equilibrated with 100 atm of hydrogen was (1.125-0.325)(1-0.005) = 0.796. With a path length of 1.004 em and an extinction coefficient of 1.1×10^4 liter $moles^{-1}$ cm^{-1} at 13,650 A[12,13] we calculated the electron eoneentration as $0.796/(1.1 \times 10^4)(1.004) = 7.20 \times 10^{-5}$ moles/liter.

Table II Equilibrium data from optical studies at 13650 Å

Molarity of Amide	Hydrogen Pressure Atm	Total Absorbance	Net* Absorbance	Concn. of Absorbing Species $\times 10^5$ (moles/liter)
2.01	0	0.325	-	-
	12.5	0.585	0.260	2.37
	25.9	0.730	0.405	3.62
	40.8	0.835	0.509	4.62
	50.3	0.900	0.573	5.20
	72.1	1.000	0.672	6.10
	87.2	1.061	0.732	6.62
	100	1.125	0.796	7.20
1.80	0	0.270	-	-
	14.3	0.589	0.319	2.92
	27.2	0.682	0.412	3.76
	53.1	0.786	0.514	4.67
	75.0	0.948	0.675	6.12
	100.0	1.045*	0.770	6.98
1.70	0	0.340	-	-
	15.0	0.640	0.300	2.75
	38.1	0.800	0.459	4.18
	64.0	0.928	0.585	5.30
	88.5	1.020	0.676	6.12
	99.7	1.043	0.698	6.32
1.85+	64.5	0.940	0.599	5.42
1.99+	42.2	0.817	0.475	4.32
2.13+	17.0	0.680	0.340	3.12

Table II (continued)

Molarity of Amide	Hydrogen Pressure Atm	Total Absorbance	Net* Absorbance	Concn of Absorbing Spec. × 10^5 (moles/liter)
1.41	0	0.339	-	-
	4.4	0.479	0.140	1.29
	9.2	0.562	0.223	2.05
	16.5	0.604	0.265	2.43
	30.0	0.700	0.360	3.29
	52.6	0.813	0.472	4.30
	74.3	0.906	0.565	5.12
	87.5	0.952	0.610	5.52
	99.7	0.994	0.652	5.90
	100.0	0.994*	0.652	5.90
1.21	0	0.323*	-	-
	0.8	0.367	0.044	0.40
	16.3	0.522	0.199	1.83
	33.3	0.647	0.323	2.95
	78	0.721	0.396	3.58
	100	0.898	0.572	5.18
1.00	0	0.216	-	-
	4.0	0.329	0.113	1.04
	11.6	0.415	0.199	1.83
	25.2	0.495	0.278	2.53
	49.0	0.618	0.401	3.65
	82.7	0.720	0.502	4.54
	99.6	0.775	0.556	5.02
	100	0.776*	0.557	5.05

Table II (continued)

Molarity of Amide	Hydrogen Pressure in Atm	Total Absorbance	Net[‡] Absorbance	Concn of Absorbing Species $\times 10^5$ (moles/liter)
0.93	0	0.233	-	-
	12.2	0.420	0.187	1.72
	18.4	0.460	0.227	2.08
	32.0	0.540	0.306	2.79
	45.0	0.592	0.358	3.25
	58.5	0.635	0.400	3.63
	72.2	0.689	0.454	4.12
	85.8	0.731	0.495	4.48
	100	0.778*	0.542	4.91
0.80	0	0.200*	-	-
	1	0.250	0.050	0.46
	12.9	0.388	0.188	1.73
	37.5	0.530	0.329	3.00
	65.0	0.635	0.433	3.93
	100	0.740	0.537	4.87
0.72	0	0.250*	-	-
$CsNH_2$*	11.5	0.390	0.140	1.29
	33.7	0.535	0.284	2.59
	61.3	0.608	0.357	3.24
	97	0.668	0.416	3.77
	100	0.700*	0.447	4.05
0.68	0	0.270	-	-
	8.85	0.402	0.132	1.21
	28.6	0.488	0.218	1.99
	49.6	0.525	0.254	2.31
	68.4	0.640	0.368	3.34
	88.0	0.660	0.388	3.51
	100	0.688	0.416	3.77

Table II (continued)

Molarity of Amide	Hydrogen Pressure Atm	Total Absorbance	Net* Absorbance	Conch of Absorbing Species $\times 10^5$ (moles/liter)
0.73+	72.0	0.644	0.372	3.37
0.79+	47.0	0.591	0.320	2.91
0.90+	18.3	0.503	0.233	2.14
0.58	0	0.245	-	-
	1.51	0.282	0.037	0.34
	14.7	0.350	0.105	0.97
	26.9	0.409	0.164	1.50
	51.4	0.478	0.232	2.11
	87.3	0.615	0.368	3.33
	98.7	0.635	0.388	3.51
	100	0.641*	0.394	3.57
0.55	0	0.300*	-	-
	0.7	0.330	0.030	0.28
	18.4	0.465	0.165	1.51
	45.2	0.557	0.276	2.51
	73.5	0.640	0.339	3.07
	95.0	0.691	0.388	3.52
	100	0.705	0.403	3.65
0.50	0	0.300*	-	-
	1.7	0.349	0.049	0.45
	18.4	0.450	0.150	1.38
	38.1	0.511	0.211	1.93
	57.1	0.583	0.282	2.56
	100	0.665	0.363	3.29
	110.2	0.670	0.368	3.33

Table II (continued)

Molarity of Amide	Hydrogen Pressure Atm	Total Absorbance	Net* Absorbance	Concentration Absorbing Species x 10^3 (moles/liter)
0.40	0	0.280	--	-
	0.56	0.307	0.027	0.25
	13.3	0.410	0.130	1.19
	24.8	0.440	0.160	1.46
	50.0	0.515	0.234	2.13
	80.0	0.576	0.294	2.67
	97.0	0.609	0.327	2.96
	100	0.615	0.333	3.01
0.28	0	0.270*	-	-
	0.3	0.277	0.007	0.06
	27.2	0.365	0.095	0.87
	74.8	0.490	0.219	1.98
	100	0.552	0.281	2.54
	111.6	0.565	0.294	2.66
0.26	0	0.268*	-	-
	1.23	0.298	0.030	0.28
	17.0	0.358	0.090	0.83
	28.3	0.420	0.152	1.39
	52.0	0.456	0.187	1.70
	82.1	0.538	0.269	2.43
	100	0.558*	0.289	2.62
	104	0.564	0.295	2.67
0.20	0	0.260*	-	-
$CsNH_2$	0.8	0.270	0.010	0.09
	11.6	0.345	0.085	0.78
	25.9	0.400	0.140	1.28
	60.5	0.462	0.201	1.83
	100	0.520*	0.259	2.37
	104	0.522	0.260	2.39

Table II (continued)

Molarity of Amide	Hydrogen Pressure Atm	Total Absorbance	Net‡ Absorbance	Concn of Absorbing Species × 10 (moles/liter
0.19	0	0.290*	-	-
	1.6	0.320	0.030	0.28
	13.6	0.377	0.087	0.80
	25.5	0.430	0.140	1.28
	57.8	0.471	0.180	1.63
	93.9	0.535	0.244	2.21
	100	0.540*	0.247	2.23
0.16	0	0.311*	-	-
	15.6	0.425	0.114	1.05
	29.3	0.466	0.155	1.42
	57.8	0.545	0.233	2.12
	78.8	0.575	0.263	2.38
	100	0.611	0.298	2.70
0.15	0	0.310*	-	-
	0.7	0.317	0.007	0.06
	20.4	0.395	0.085	0.78
	39.1	0.427	0.117	1.07
	60.5	0.452	0.141	1.28
	93.2	0.472	0.161	1.46
	100	0.496*	0.185	1.67
.067	0	0.270*	-	-
	11.5	0.329	0.059	0.54
	28.3	0.370	0.100	0.91
	61.5	0.397	0.126	1.15
	95.0	0.412	0.141	1.28
	100	0.438*	0.167	1.51
	110	0.445	0.174	1.58

Table II (continued)

Molarity of Amide	Hydrogen Pressure Atm	Total Absorbance	Net* Absorbance	Solubility of N_2 - concentration fraction $\times 10^5$ (moles/liter)
.027	0	0.256	-	-
$NaNH_2$	25.8	0.263	0.007	0.06
	49	0.270	0.014	0.13
	67	0.276	0.020	0.18
	100	0.277	0.021	0.19
	58+	0.274	0.018	0.17
	24.5+	0.260	0.004	0.04

* Determined by extrapolation of the measured absorbance

\+ The hydrogen pressure was reduced to test the reversibility of the equilibrium. The amide concentration was adjusted for loss of ammonia.

‡ Value corrected for the change in density of the solution.

Figure 4 shows the relationship between the electron concentration and the hydrogen pressure at several amide concentrations. The data at all concentrations studied exhibited the same linear dependence on the square root of the hydrogen pressure. To determine whether it was the hydrogen pressure or just pressure alone which caused the increase in absorbance, the following experiment was performed. The spectrum at a 25 atm hydrogen pressure was recorded, then, using an inert gas, the pressure was increased by 25 atmospheres and the spectrum again recorded. The experiment was repeated several times using helium, argon, and nitrogen. No increase in absorbance other than that due to changing path length and density was detected. To ensure that nothing had affected the sample during the experiment, hydrogen was again added to the system and the spectrum recorded. An increase in absorbance was detected in every case.

From the data in Table II at 100 atmospheres of hydrogen pressure, assuming the amide to be completely dissociated, we calculated an equilibrium quotient for reaction (1) from the equation

$$K_c = \frac{[NH_2^-]\ P_{H_2}^{1/2}}{[e_{am}^-]}$$

The result is curve K_c, Fig. 5. Unfortunately these data do not yield a constant value for K_c. To try to resolve this difficulty we treated the data in two ways.

A modified Debye-Hückel treatment was employed combining the properties of KNH_2 in liquid ammonia calculated by Fuoss and Kraus[20] with the calculations for an alkali metal made by Arnold and Patterson.[20] This treatment required a series of approximations not the least of which was that the Debye-Hückel theory was valid at these concentrations.

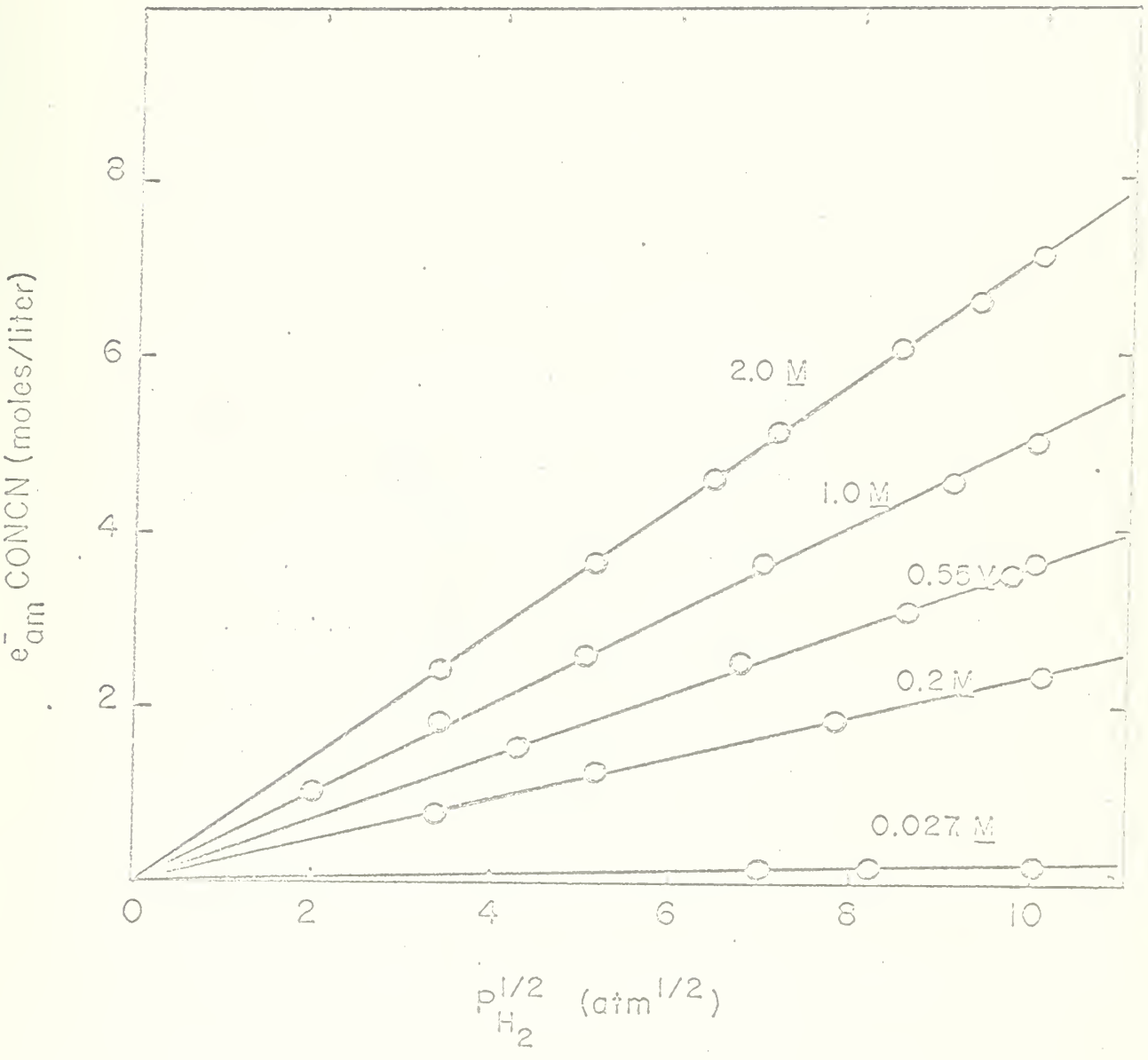

Fig. 4 Electron Concentration vs the Square Root of the Hydrogen Pressure at Several Amide Concentrations as Determined by Optical Measurements.

Most measurements in liquid ammonia were made at -33° and it was necessary to correct all values to 25°. Based on the heat of dilution for KI and other salts in liquid ammonia measured by Gunn and Green,[5] we estimated the heat of dissociation of KNH_2 ion pairs as -3.5 kcal and by applying the vant Hoff equation:

$$-\Delta H = \frac{R \ln K_2/K_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

to the value $K_D = 0.7 \times 10^{-4}$ at -33° as determined by Fuoss and Kraus[20] we calculate a value of $K_D = 2 \times 10^{-5}$. Using this value, and a value for the dielectric constant of ammonia equal to 16.9 at 25°[22] we calculated the degree of dissociation and activity coefficients for KNH_2 at concentrations from 0.01 to 2.9M. By assuming the principle of ionic strengths and estimating a dissociation constant of 2×10^{-2} for the reaction[21,23,24]

$$K = K^+ + e^-$$

we calculated a value for (e^-) and activity coefficients for potassium in liquid ammonia. It was assumed that the concentrations of other species such as K_2 and K^- were negligible. Trial values calculated from estimated dissociation constants and activity coefficients indicate that this last assumption was reasonably valid. The activity coefficients of uncharged species were assumed to be unity. This calculation failed to produce a significant improvement in the data. Details of this calculation are shown in Appendix D.

Finally, an equilibrium constant was calculated from the equation

$$K = \frac{[KNH_2]\, \gamma_{\pm}^2\, p^{1/2}}{[e^-]\, \gamma_{\pm}^2}$$

where it was assumed that the empirically determined mean ionic activity coefficient included the effect of ion pairing. Since no activity coefficient data had been reported for any of the alkali amides, values were estimated from the measurements on NH_4Cl at 25° by Pitchie and Hunt.[25] The activity coefficients for potassium were taken from the work of Marshall.[26] The latter values were measured at -33° and were left uncorrected. The results of this calculation appear in Table III and as curve K, Fig. 5. Obviously this last treatment is a real improvement over the previous calculations.

The value of K for reaction (1) obtained by extrapolating the last set of calculations to zero concentration is approximately 5×10^{-4}. A value of $K = 3 \times 10^{9}$ was calculated for reaction (2) from the data for a saturated $NaNH_2$ solution using the expression

$$K = \frac{p_{H_2}^{1/2}}{[Na^+][e^-]\,\gamma_\pm^2} \quad .$$

Table III. Determination of the equilibrium constant using estimated activity coefficients $P_{H_2} = 1.00$ atm

Amide Conc.	$\gamma_\pm$ of Amide	$\gamma_\pm$ of Metal	Adjusted Electron Conc.	K'_{eq}
2.0	1.35×10^{-2}	2.90×10^{-2}	6.6×10^{-5}	6.6×10^{4}
1.8	1.50	2.95	6.5	7.2
1.7	1.57	3.00	5.9	7.9
1.4	1.82	3.25	5.5	8.1
1.2	1.97	3.55	4.8	7.7
1.0	2.25	4.00	4.7	6.8
0.93	2.37	4.25	4.5	6.4
0.80	2.65	4.70	4.5	5.7
0.72	2.91	5.05	3.7	6.2
0.68	3.03	5.25	3.5	6.5
0.58	3.55	5.75	3.3	6.7
0.55	3.75	6.05	3.3	6.2
0.50	4.05	6.35	3.0	6.7
0.40	4.45	7.05	2.7	6.2
0.28	6.10	9.25	2.3	5.3
0.26	6.35	9.50	2.4	4.8
0.20	7.72	10.5	2.1	5.2
0.19	8.70	11.0	2.0	6.0
0.16	9.80	11.7	2.5	4.7
0.15	10.5	12.0	1.5	7.6
0.067	18.0	18.5	1.4	4.7
0.027	-	27.0	0.18	3×10^{9}

$\pm$ $CsNH_2$

$\pm$ $NaNH_2$

$[e^-] = \dfrac{S}{1 + (K^+)\gamma_\pm^2/\gamma_1}$ S = conc. of absorbing species from Table II

$K_{eq} = 2 \times 10^{-2}$

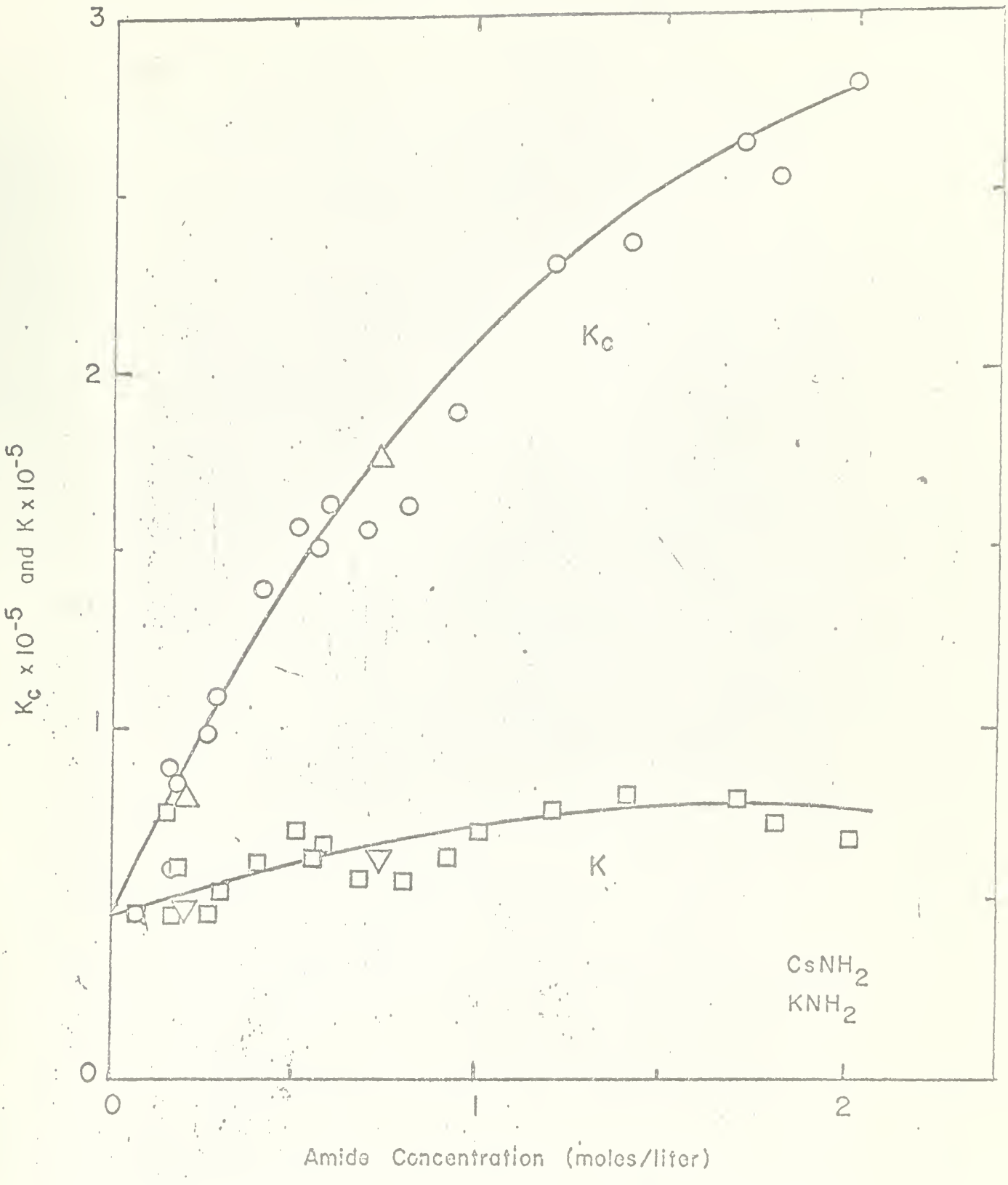

Fig. 5 K_c and K vs Amide Concentration for Reaction (1) from Optical Measurements

$$K_c = \frac{[NH_2^-]\, P_{H_2}^{1/2}}{[e^-]} \qquad K = K_c \frac{\gamma^2_{\pm MNH_2}}{\gamma^2_{\pm M}}$$

V. RESULTS OF THE EPR MEASUREMENTS

A. Determination of An Equilibrium Quotient

As previously reported,[27] we attempted to measure the equilibrium constant of reaction (1) using EPR. In the earlier work we found almost direct dependence of the equilibrium quotient on the concentration of KNH_2. At the time it was believed that a decrease in sensitivity of the spectrometer was responsible. The later experiments utilized smaller diameter sample tubes in an attempt to correct the problem. Table IV shows the results. The equilibrium quotient was calculated both with and without the use of estimated activity coefficients and plotted as Fig. 6. Extrapolation to zero concentration yields a value of approximately 5×10^4 which is in good agreement with the optical data.

Several experiments were carried out to try to resolve the amide dependence. In one test various amounts of KBr were added to a saturated $NaNH_2$ solution at constant hydrogen pressure to determine the effect of chaning ionic strength on the system. The results are shown in Table V. The electron concentration decreases with increasing ionic strength.

One would expect that the effect on reaction (2) of increasing the ionic strength would be to decrease the activity coefficient of the ammoniacal electron and in order for the activity of the electron to remain constant its concentration would increase. The trend observed here is the reverse of that and the only possible explanation we can offer at this time is that it is due to a decrease in the sensitivity of the spectrometer caused by the high salt concentration. We were not able to assign any further significance to this result.

Another experiment was performed using varying concentrations of

Table IV. Equilibrium data from EPR Experiments

Concentration of Amide (moles/liter)	Hydrogen Pressure (Atm)	Concentration of Electrons (moles/liter)	$Q = \frac{P_{H_2}^{1/2}(NH_2^-)}{(e^-)}$	$^{*}K_{eq} = Q\frac{\gamma_{\pm}^2(KNH)}{\gamma_{\pm}^2(K)}$
0.269	7.52	4.50×10^{-6}	1.65×10^{-5}	0.70×10^{-5}
0.361	18.9	8.05	1.96	0.81
0.815	19.2	9.24	3.87	1.24
1.00	19.4	9.92	4.44	1.35
1.08	16.8	8.45	5.26	1.58
2.40	21.5	13.0	8.55	1.41

* $\gamma_{\pm}(KNH_2)$ estimated from reference 25.

$\gamma_{\pm}(K)$ from reference 26.

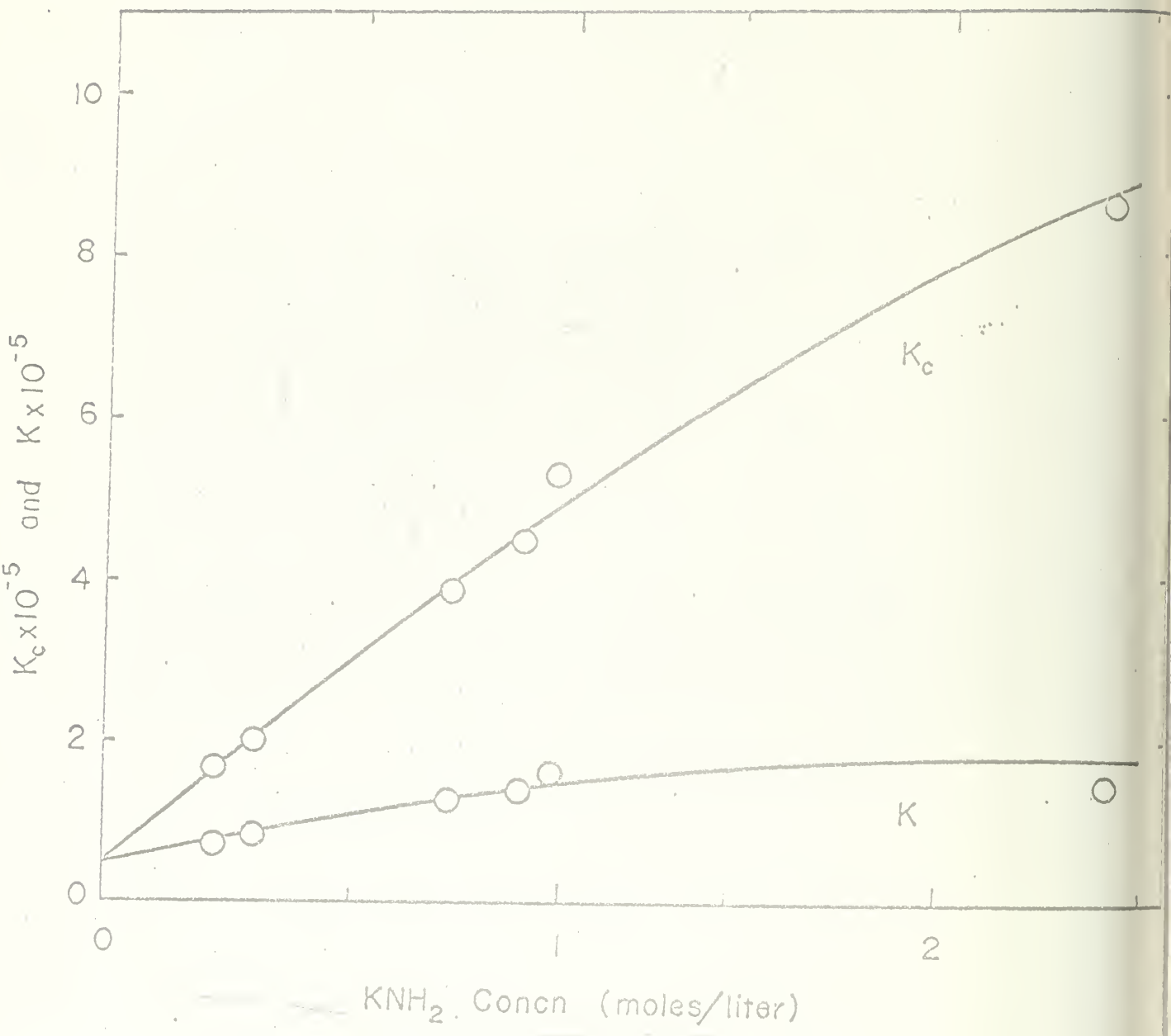

Fig. 6 K_c and K vs KNH_2 Concentration for Reaction (1) from EPR Measurements

$$K_c = \frac{[NH_2^-]\, P^{1/2}}{[e^-]} \qquad K = K_c \frac{\gamma^2_{\pm KNH_2}}{\gamma^2_{\pm K}}$$

Table V. Effect of Changing Ionic Strength on the EPR Signal of a Saturated Solution of NaBr in Equilibrium with Hydrogen

Molarity of KBr Added	Hydrogen Pressure (Atm)	Relative Signal Strength
0	24.0	1.59
0.2	25.0	1.19
0.1	26.0	1.07
0.2	25.5	1.01
0.58	25.4	1

KNH_2 and attempting to keep the ionic strength constant with KBr. The results are shown in Table VI. The psuedo equilibrium quotient shown in the last column failed to remain constant. However, the trend of the change in this value is the reverse of that in the equilibrium study in Table IV. The value of the equilibrium quotient increases with decreasing amide concentration. Unfortunately we were again faced with the problem of predicting true ionic strength without a knowledge of the degree of dissociation at room temperature.

If we conclude that the KBr is more dissociated than KNH_2 then we see that the ionic strength increased when the KBr/KNH_2 ratio increased resulting in an increase in the dielectric strength of the sample and a loss in sensitivity.

The final experiment attempted to show that the law of mass action was obeyed. Here we kept the ionic strength constant by using a high concentration of KBr. Various amounts of NaBr were then added to a saturated solution of $NaNH_2$. Table VII shows the results. The electron concentration decreases with the addition of sodium ion as would be predicted, however, the equilibrium quotient calculated on the basis of the equation

$$Na^+ + e^- + NH_3 = NaNH_{2(c)} + \frac{1}{2}H_2$$

is still not constant. This may be due to an error in the ionic strength value used in selecting values for the activity coefficient from the data of Marshall.[26] The ionic strength was considered to be constant and to equal the sum of the concentrations of KBr and NaBr and because of the lack of data at 25°, the difference in the degree of dissociation of the two salts was not taken into account.

Table VI. Changing KNH_2 concentration with total potassium constant

Concentration KNH_2	Concentration KBr	Hydrogen Pressure	Relative Signal Intensity, S	$S/P_{H_2}^{1/2}$	$\frac{(NH_2^-)P^{1/2}}{S}$
1.01	0	24.1	1.65	0.34	3.0
0.84	0.10	23.0	1.38	0.29	2.9
0.79	0.20	20.4	1.01	0.22	3.5
0.65	0.30	20.6	1.00	0.22	3.0
0.63	0.40	23.5	0.80	0.16	3.8
0.49	0.50	22.7	0.55	0.12	4.3

Table VII. Effect of adding a common ion at constant ionic strength

M NaBr Added	Relative Signal Intensity, S	Hydrogen Pressure Atm.	Na^+ Conc. (Calc.)	$S/P^{1/2}$	$\frac{* P^{1/2}}{(Na^+)(S)\gamma_{\pm Na}^2}$
0	4.40	23.0	0.027	0.92	1.2×10^4
0.013	4.00	18.8	0.033	0.92	0.87
0.017	4.00	20.6	0.034	0.88	0.83
0.027	3.90	21.0	0.042	0.85	0.75
0.047	3.30	21.0	0.058	0.72	0.63
0.112	1.70	20.5	0.117	0.38	0.62
0.233	0.97	27.7	0.236	0.018	0.61

* $\gamma_{\pm(Na)}^2$ from reference 26

In these last three experiments we used relative signal intensities, which are proportional to the electron concentration, in our calculations rather than attempting to measure the absolute value of the electron concentration.

B. Pressure Dependence Studies Using ESR

Two runs were made using ESR to verify the pressure dependence results found by optical methods. In the first, 1M KNH_2 solutions were prepared in such a way as to vary the hydrogen pressure. This was accomplished by simply keeping the weight of potassium and the volume of ammonia in each sample constant and varying the total volume of the tube. The second set of experiments were run using saturated $NaNH_2$ solutions. Here the volume of the tubes and the quantity of ammonia were kept constant and the quantity of metal varied. The results are shown in Table VIII. In both cases the intensity of the spectrum was linearly dependent upon the square root of the hydrogen pressure.

C. Temperature Dependence of the Equilibrium

The temperature dependence of the equilibrium of reaction (1) was studied for three different concentrations of KNH_2 and of reaction (2) for a saturated solution of $NaNH_2$. The results are shown in Table IX.

We treated the data by using the ratio of the signal intensity at a given temperature to that at a base temperature to calculate the ratio of the equilibrium quotients K_{rt}/K where the subscript rt denotes the base temperature. We used ambient temperature as a base because it could be easily controlled by a simple adjustment of the air flow around the sample and did not require the adjustment of the thermostat.

The signal intensity value had to be corrected for the change in

Table VIII. Hydrogen pressure dependence

Hydrogen Pressure	Signal Intensity	Electron Concentration	Equilibrium Constant
	1M KNH_2 Solution		
35.5	5.70	13.1×10^{-6}	1.5×10^{5} †
29.0	4.92	11.3	1.6
19.4	4.32	9.92	1.5
16.8	3.68	8.43	1.6
10.0	2.87	6.60	1.6
	Saturated $NaNH_2$ Solution (0.027M)		
38	0.418	0.94×10^{-6}	3.3×10^{9} ‡
34	0.382	0.87	3.4
25	0.310	0.71	3.6
22	0.316	0.71	3.4
19	0.281	0.64	3.4
14	0.243	0.56	3.4

† From the expression $$K = \frac{[NH_2^-]\ \gamma_{\pm}^2\ P_{H_2}^{1/2}}{[e^-]\ \gamma_{\pm}^2}$$

‡ From the expression $$K = \frac{P_{H_2}^{1/2}}{[Na^+][e^-]\gamma_{\pm}^2}$$

The activity coefficients were estimated from References 25 and 26

the Boltzmann distribution of the energy levels with changing temperature. At a given temperature the distribution ratio is written

$$\frac{N_2}{N_1} = \frac{\exp(-E_2/kT)}{\exp(-E_1/kT)} \quad \text{or} \quad \frac{N_2}{N_1} = \exp - \frac{\Delta E}{kT}$$

and by expanding we get

$$\frac{N_2}{N_1} = 1 - \frac{\Delta E}{kT} + \frac{\Delta E^2}{2!(kT)^2} - \frac{\Delta E^3}{3!(kT)^3} + \cdots\cdots$$

ΔE is small compared to kT so neglecting higher order terms and rearranging we get

$$N_2 - N_1 = N_1 \frac{\Delta E}{kT}$$

N_2-N_1 is proportional to the signal intensity so as an approximation we corrected the intensity value by multiplying by the ratio T/T_{rt}.

The ratio of the equilibrium quotients for reaction (1)

$$\frac{K_{rt}}{K} = \frac{[e^-_{am}]}{[e^-_{am}]_{rt}} \frac{[NH_2^-]_{rt}}{[NH_2^-]} \frac{P_{rt}^{1/2}}{P^{1/2}}$$

had to be corrected for the change in the hydrogen pressure with temperature and the change in the NH_2^- concentration due to the change in the density of the solution. The pressure correction was made assuming hydrogen behaves ideally and considering the change in solubility of hydrogen in liquid ammonia with changing temperature and pressure.[19] See Appendix B. The NH_2^- concentration is directly proportional to the density of the solution, therefore, density was substituted for the NH_2^- concentration in the expression for K_{rt}/K. As an estimate of the density of the solution we used the density of liquid ammonia.[16] The expression

for reaction (1) was

$$\frac{K_{rt}}{K} = \left(\frac{S}{S_{rt}}\right)\left(\frac{T}{T_{rt}}\right)\left(\frac{D_{rt}}{D}\right)\left(\frac{P_{rt}}{P}\right)^{1/2}$$

where S equals the observed signal intensity, T the temperature in °K, P the hydrogen pressure in atmospheres and D the density of the solution.

The ratio K_{rt}/K was plotted against $1/T$ and is shown in Fig. 7 and Fig. 8. We calculated the slope using the vant Hoff equation:

$$\Delta H = \frac{R \ln \frac{K_{rt}/K_2}{K_{rt}/K_1}}{1/T_2 - 1/T_1} = \frac{R \ln K_1/K_2}{1/T_2 - 1/T_1}$$

This gave a value of -15.7 kcal. It is interesting that the heat of reaction appears to be independent of concentration.

The value -15.7 kcal is a measure not only of reaction (1) but also of the contribution of the heat of dissociation of the ion pair $K^+NH_2^-$. No one has measured this heat of dissociation so in order to calculate the heat of reaction (1) we had to estimate a value. From the heat of solution of KI in liquid ammonia determined by Gunn and Green[5] we obtained a value of -3.5 kcal for the heat of dilution of KI. By assuming that KNH_2 would have a comparable value and assuming that the KNH_2 is mostly ion paired ($K_D \sim 2 \times 10^{-5}$) we calculated the heat of reaction (1) as

$$K^+NH_2^- = K^+ + NH_2^- \qquad \Delta H = -3.5 \text{ kcal}$$

$$K^+ + e^-_{am} + NH_3 = K^+NH_2^- + 1/2H_2 \qquad \Delta H = -15.7 \text{ kcal}$$

$$e^- + NH_3 = NH_2^- + 1/2H_2 \qquad \Delta H = -19.2 \text{ kcal}$$

The ratio of the equilibrium quotients for reaction (2) is:

$$\frac{K_{rt}}{K} = \frac{[e^-_{am}] \quad [Na^+] \quad P_{rt}^{1/2}}{[e^-_{am}]_{rt} \; [Na^+]_{rt} \; P^{1/2}}$$

We corrected this expression for the temperature change in the same way as for reaction (1) and obtained

$$\frac{K_{rt}}{K} = \left(\frac{S}{S_{rt}}\right)\left(\frac{T}{T_{rt}}\right)\left(\frac{D}{D_{rt}}\right)\left(\frac{P_{rt}^{1/2}}{P^{1/2}}\right)$$

This ratio was plotted against 1/T in Fig. 8 and the slope determined to give a $\Delta H = -12.3$ kcal. By estimating the heat of solution of $NaNH_2$ as approximately zero we calculated a value for reaction (1) as:

$$NaNH_{2(c)} = Na^+ + NH_2^- \qquad \Delta H = +0 \text{ kcal}$$

$$Na^+ + e^- + NH_3 = NaNH_{2(c)} + 1/2H_2 \qquad \Delta H = -12.3 \text{ kcal}$$

$$e^- + NH_3 = NH_2^- + 1/2H_2 \qquad \Delta H = -12.3 \text{ kcal}$$

This value does not agree with the value calculated from the data for the KNH_2 solutions but does agree with that estimated from other thermodynamic data, -12 kcal.

Table IX Temperature dependence

Temp °K	Signal Intensity	S_T/S_{rt} +	Temp Correction	Pressure Correction	Density Correction	K_T
			0.85M KNH_2 Run 1			
294.7	1.26	1	1	1	1	1
309.4	4.40	3.50	1.045	0.979	1.035	3.7
317.7	10.45	8.24	1.072	0.960	1.055	8.9
333.9	24.40	19.35	1.130	0.935	1.090	22.3
320.0*	9.6	7.6	1.060	0.962	1.060	8.4
			0.85M KNH_2 Run 2			
294.7	2.09	1	1	1	1	1
280.9	0.334	1.160	0.950	1.025	0.970	0.1
265.7	0.100	0.048	0.910	1.050	0.945	0.0
			0.85M KNH_2 Run 3			
324.7	17.20	9.07	1.100	0.953	1.072	10.20
316.0	9.70	5.10	1.070	0.966	1.050	5.9
308.0	5.85	3.08	1.045	0.980	1.032	3.26
303.3	3.72	1.96	1.028	0.985	1.020	1.98
294.7	1.90	1	1	1	1	1
			1.05M KNH_2			
271.2	1.96	0.100	0.920	1.041	0.950	0.09
274.2	2.60	0.133	0.932	1.035	0.956	0.12
278.2	3.94	0.201	0.943	1.030	0.965	0.18
283.2	6.28	0.321	0.960	1.020	0.974	0.30
283.9	7.30	0.373	0.961	1.020	0.977	0.35
290.5	13.20	0.674	0.985	1.010	0.993	0.66
294.2	19.20	0.980	0.999	1	0.999	0.97
294.7	19.60	1	1	1	1	1

Table IX (Continued)

Temp °K	Signal Intensity	S_T/S_{rt} +	Temp Correction	Pressure Correction	Density Correction	K_{rt}/K
			2.01M KNH_2			
272.9	1.80	0.135	0.927	1.040	0.954	0.124
280.2	3.22	0.240	0.950	1.025	0.970	0.225
288.0	6.77	0.506	0.970	1.020	0.985	0.492
294.5	13.41	1	1	1	1	1
			Saturated $LiNH_2$			
296.2	36	1	1	1	1	1
301.2	50.5	1.40	1.015	0.992	0.988	1.39
306.2	68	1.86	1.035	0.982	0.976	1.84
313.2	99.5	3.02	1.058	0.971	0.960	2.98
317.2	56	4.05	1.071	0.965	0.950	3.99
304.2*	65	1.65	1.027	0.986	0.982	1.74
300.7*	48	1.33	1.015	0.992	0.989	1.32

+ Room Temperature of KNH_2 Runs 294.7 °K
$NaNH_2$ Runs 296.2 °K

* Direction of Temperature Change Reversed

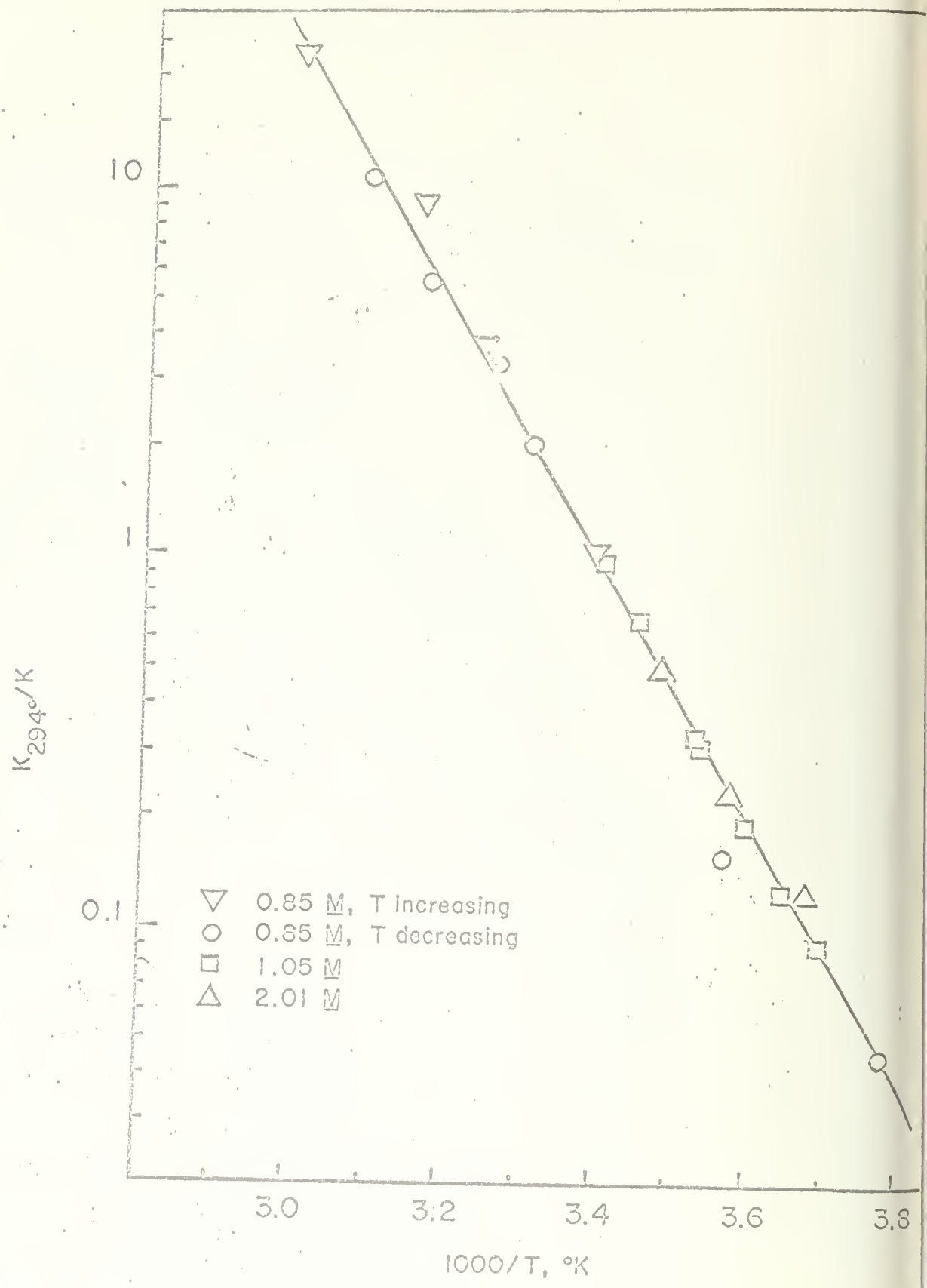

Fig. 7 Log of the Ratio $K_{294°}/K$ vs 1/T for Solutions of KWH_2 in Equilibrium with Hydrogen

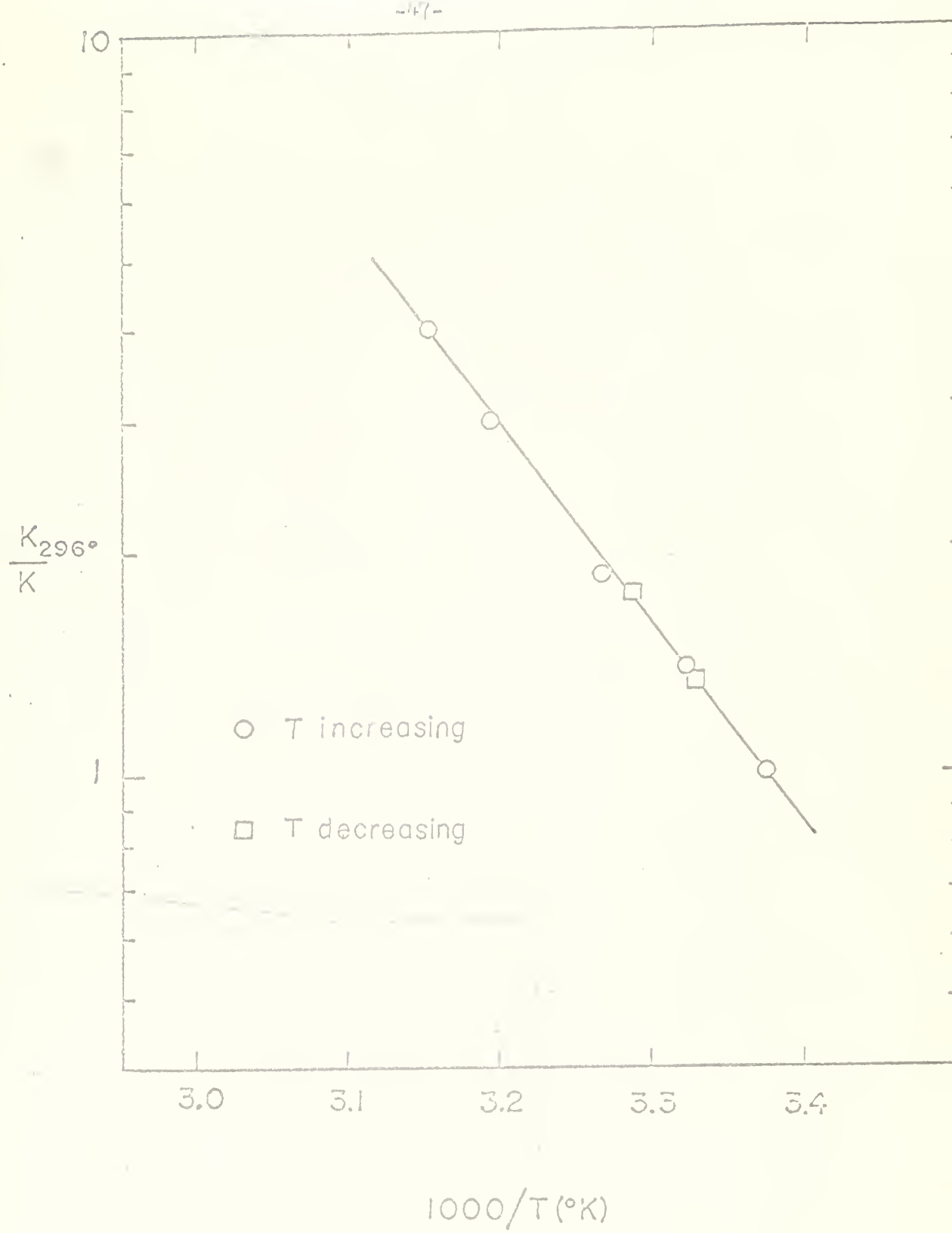

Fig. 8 Log of the Ratio $K_{296°}/K$ vs 1/T for a Saturated Solution of $NaNH_2$ in Equilibrium with Hydrogen and Solid $NaNH_2$

VI. DISCUSSION

The most consistent result in this investigation was the effect of hydrogen pressure on the system. Without exception, the electron concentration at a given amide concentration was directly proportional to the square root of the hydrogen pressure. This result agrees exactly with the stoichiometry of the reaction of an alkali metal with liquid ammonia.

The effect of the amide concentration was more complex. It is apparent from the data that activity coefficients have a strong effect on the equilibrium.

The expression for the thermodynamic equilibrium constant of (1) is

$$K = \frac{[NH_2^-]\,\gamma_{-1}\,P_{H_2}^{1/2}\,\gamma_{H_2}}{[e^-]\;\;\gamma_{-2}}$$

We assumed $\gamma_{H_2} = 1$ and this left a ratio of the activity coefficients of two negative species. We at first assumed that this ratio approached unity even at concentrations as high as 1M. Our data indicate that this assumption is not valid. If one considers the size effect of an ion in a solvent of low dielectric strength we can qualitatively explain this result. The ammoniated electron is usually considered to behave as a large negative ion while the amide ion in liquid ammonia has been concluded to have a small effective radius.[29]

In most of the common theories of electrolytes[30] this size parameter has an effect on the calculated value of the activity coefficient. If we consider the degree of dissociation of the ionic species to be an indication of the specific ionic interactions, we can use as further evidence of a difference in the activity coefficients the fact that the

dissociation constant of potassium in liquid ammonia is approximately 10^{-2} while that for KNH_2 is 10^{-5}.

The application of the Debye-Hückel theory to our data failed to produce an equilibrium quotient which was constant at all amide concentrations. It did however result in some improvement in the curve in Fig. 5. The use of activity coefficients estimated from empirical data produced an even larger improvement. We believe that with the proper values for the activity coefficients the concentration effect could be accounted for.

The measurement of the equilibrium by EPR was hampered by the effect of the dielectric strength on the sensitivity of the instrument and by the lack of accurate dissociation constant for salts at 25°. By extrapolating the data to zero amide concentration we did obtain a value in agreement with the optical data. Considering the accuracy of measuring the electron concentration by this method (~ ± 50%) the result is rather fortuitous. It does at least indicate the order of magnitude of the equilibrium constant and when considered with the optical data we evaluated the equilibrium constant as approximately 5×10^4 for reaction (1).

The expression for the equilibrium quotient of reaction (2) is

$$K = \frac{p^{1/2}}{(Na^+)\ (e^-)\ (\gamma_{\pm}^2)}$$

From the EPR data of Table VII we determined a value of $K = 3.4 \times 10^9$. Using the data of Table II, which was obtained optically, we calculate $K = 3 \times 10^9$. This is in remarkably good agreement considering the inaccuracy of the optical data due to the low net absorbance of the samples.

The temperature dependence of the two systems resulted in a comparable heat of reaction for the overall reactions (3) (4) but when an attempt was made to calculate the heat of reaction (1) $e^- + NH_3 = NH_2^- + \frac{1}{2}H_2$ the results diverged. The lack of sufficient thermodynamic data precludes any further treatment of this problem at this time.

The difference between reaction (1) and reaction (2) is the dissolution reaction of $NaNH_{2(c)}$

$$e^- + NH_3 = NH_2^- + 1/2H_2 \qquad (1)$$

$$\underline{Na^+ + e^- + NH_3 = NaNH_{2(c)} + 1/2H_2} \qquad (2)$$

$$NaNH_2 = Na^+ + e^-$$

Therefore, the ratio of the equilibrium constants of reaction (1) and (2) is the solubility product of the $NaNH_2$ solution. Calculating K_s from the concentration of a saturated solution of $NaNH_2$ (0.027M) and an estimated value of the activity coefficient $(0.27)^{25}$ we obtained $K_s = 5 \times 10^{-5}$. Our data resulted in a value of $K_s = 5 \times 10^4/3 \times 10^9 = 1.7 \times 10^{-4}$ which is in fair agreement with the value determined from the solubility data.

APPENDIX A

Calculation of the Amide Concentration of the Optical Samples

In the determination of the amide concentration of the optical samples from the weight of the metal and ammonia used, we had to account for that fraction of the ammonia which was in the gas phase. This often amounted to about 15% of the weight of ammonia used. The following example illustrates this calculation.

The volume of the cell plus the gage was determined to be 20.24 cc. 1.290 grams of ammonia and 0.0325 grams of potassium metal were used in the sample. The potassium reacted with the ammonia to form 0.832 millimoles of KNH_2. The density of solid KNH_2 is 1.64 g/cc[16] and the density of ammonia at 25° is 0.6028 g/cc.[22] By estimating the change in volume of the solution due to the added KNH_2 from the density of solid KNH_2 we calculate

$$V = \frac{1.290 \text{ g}}{0.6028 \text{ g/cc}} + \frac{55.1 \text{ g/mole} \times 0.832 \times 10^{-3}}{1.64 \text{ g/cc}} = 2.17 \text{ cc}$$

The volume of the gas space was estimated to be 20.24-2.17 = 17.07 cc. The vapor pressure of the ammonia was estimated from Raoult's Law. The mole fraction of ammonia in solution is 0.99 and the vapor pressure of pure ammonia at 25° is 9.9 atm. The partial pressure of the ammonia in the solution is (0.99) (9.9) = 9.8 atm. Substituting these values in the van der Waal equation[15]

$$\left(P + \frac{4.170\ n_g^2}{V^2}\right)(V - 0.0371\ n_g) = nRT \qquad (A\text{-}1)$$

$$\left(9.8 + \frac{4.170\ n_g^2}{(0.0181)^2}\right)(0.0181 - 0.0371\ n_g) = 24.4\ n_g$$

We calculated the value of n_g by successive approximations. The value obtained in this first step, 0.0072 moles was used to obtain a value for the volume of the solution and the entire procedure was repeated. The second volume was 1.96 cc which gave a net volume of the gas space equal to 18.3 cc. Substituting in (A-1) we get n_g = 0.0077 moles. The volume of the liquid calculated from this value is

$$2.17 \text{ cc} - (0.0077)\ (17.031)/1.64 = 2.09 \text{ cc}$$

and the net volume of the gas space is 20.24 - 2.09 / 18.15 cc. By substituting in (A-1) we calculate n_g = 0.0076 moles. The volume of the solution was then calculated to be 2.09 cc. The concentration of the KNH_2 was then 0.832/2.09 = 0.398 M.

APPENDIX B

Details of the Determination of Hydrogen Pressure and Amide Concentration for the EPR Samples

The number of moles of hydrogen n_T produced by the reaction:

$$M + NH_3 = MNH_2 + \frac{1}{2} H_2 \qquad (B\text{-}1)$$

was determined for each sample as previously described. The total hydrogen can be expressed as

$$n_T = n_G + n_L \qquad (B\text{-}2)$$

where n_G is the number of moles of hydrogen in the gas phase and n_L the number of moles dissolved in the solvent. Assuming that the effect of the added salt on the solubility of hydrogen is negligible, and that hydrogen behaves ideally at the temperatures and pressures studies, we determined n_L and n_G. From a plot of the data for the solubility of hydrogen in liquid ammonia given by Wiebe and Tremaerne[19] we obtained a value

$$k = \left(\frac{\Delta V}{\Delta P} \right)_T \qquad (B\text{-}3)$$

where V is the volume in cc's of hydrogen at standard temperature and pressure dissolved in one gram of NH_3 per atmosphere of hydrogen partial pressure. Applying the ideal gas law, the amount of hydrogen in solution can be expressed as:

$$n_L = \frac{k}{22,400} P_{H_2} W_{NH_3} \qquad (B\text{-}4)$$

where W_{NH_3} is the weight of NH_3 in grams. If the measured volume of liquid was used instead of the weight, then we substituted $V_{NH_3} \cdot d_{NH_3}$ for

W_{NH_3} where V_{NH_3} is the volume of the solution minus the volume of the amide based on the density of the density of the solid amide. A comparison of the value for pressure obtained using weight against the value using volume on a given sample agreed to within 5%. From the ideal gas approximation

$$n_G = \frac{V_{H_2} P_{H_2}}{82.06T} \tag{B-5}$$

and

$$n_T = n_G + n_L = \frac{V_{H_2} P_{H_2}}{82.06T} + \frac{k}{22,400} P_{H_2} W_{NH_3} \tag{B-6}$$

Rearranging we get

$$P_{H_2} = \frac{n_T}{\left(\frac{V_{H_2}}{82.06T}\right) + \left(\frac{k}{22,400} W_{NH_3}\right)} = \frac{n_T}{\left(\frac{1}{82.06T} V_{H_2}\right) + \left(\frac{kd_{NH_3}}{22,400}\right) V_{NH_3}} \tag{B-7}$$

At 25° the above expression reduces to

$$P_{H_2} = \frac{n_T \times 10^5}{4.10 V_{H_2} + 0.291 V_{NH_3}} \tag{B-8}$$

The volume of the gas space was determined as the total volume of the sample tube minus the volume of the solution and any undissolved amide in the tube. The volume of the solution was determined by weight and, if possible, by direct measurement of the height of the liquid in the sample tube (of known cross sectional area).

In all of the EPR experiments the ratio of the gas volume to the liquid volume was less than 0.5 and we assumed the amount of NH_3 in the gas phase with respect to the liquid phase to be negligible. When the weight of NH_3 was used to determine the volume of the solution, the

volume of the solution, the volume of the amide, based on its density as a solid, was added to the volume of pure NH_3 calculated from its density. The concentration of amide in the sample solution was then determined by

$$[MNH_2] = 2n_{H_2}/V \text{ (solution)} \qquad (B\text{-}9)$$

In the following example we calculated the hydrogen pressure and amide concentration for the 1 M sample of Table IV.

The total number of moles of hydrogen, n, was determined from the measurement described under the experimental section. The volume of the gas buret was 9.65 cc and the hydrogen pressure was 307 mm and from the ideal gas assumption we calculate $n_T = 0.162 \times 10^{-3}$ moles. The cross section of the sample tube was 0.0227 cm^2 and the total length was 22.12 cm. The total volume of the tube equalled 0.502 cm^3. The height of the liquid in the tube was 14.20 cm and its volume was 0.322 cm^3. By difference the volume of the gas space was 0.180 cm^3. Substituting in (B-8)

$$P_{H_2} = \frac{(0.161 \times 10^{-3})\ 10^{-5}}{(4.10)(0.180)+(0.291)(0.322)} = 19.4 \text{ atm}$$

The amide concentration was calculated from (B-9) and equals 1 - 0 M.

APPENDIX C

Calculation of the Electron Concentration from EPR Results

The intensity of the EPR spectrum of a solution of alkali metal amide in liquid ammonia in equilibrium with hydrogen was compared to a benzene solution of recrystallized vanadium (IV) oxyacetylacetonate of known concentration. The effect of the two different solutions on the Q value of the cavity was accounted for by means of an intermediate standard of solid diphenylpicrylhydrazyl.

The intensity of a resonance may be approximated by:

$$I = KW^2H \qquad (C\text{-}1)$$

where W is the peak to peak separation of the derivative and H is the height of the resonance. The constant K is determined by the line shape and some of the values are as follows:

Lorentzian Line	1.81
Gaussian Line	0.52
DPPH	1.1

The shape of the VO^{++} line is Lorentzian while that of the electron in the metal amide solution approaches a Gaussian shape. A value of K = 1 was estimated for the electron line.

In order to use the equation (C-1), the modulation amplitude used in obtaining a resonance must be less than 50% of the line width. This limitation required the use of different modulation amplitudes for the electron and the VO^{++}. If the modulation amplitude is less than 50% of the line width, then the signal intensity is proportional to the modulation amplitude. The signal was corrected by dividing by the modulation amplitude M.

The intensity of the resonance was corrected for the change in the Q of the cavity by dividing by D, the corresponding DPPH signal intensity

$$I = \frac{KW^2H}{MD} \qquad (C\text{-}2)$$

The concentration of the electron was calculated from the expression

$$[e^-] = [VO^{++}] \frac{I_{e^-}}{I_{VO^{++}}} \qquad (C\text{-}3)$$

The data used to calculate the electron concentrations in Table IV are shown in Table C-I. All units except concentration cancel in (C-3), therefore we used relative scale values for H, W, and D.

The concentration of VO^{++} was 1.86×10^{-2} M. Its spectrum consists of 8 lines of equal intensity. At a modulation amplitude, M = 100, we measured H = 43.7 and W = 8 for one line. The corresponding DPPH signal had an intensity D = 50. Substituting these values in (C-2) and multiplying by eight to account for the total intensity of all 8 lines we get

$$I_{VO^{++}} = \frac{(8)\,(1.81)\,(8)^2\,(43.7)}{(100)\,(50)} = 8.10$$

Using (C-3) the electron concentration of the 1 M sample in Table C-I was calculated as follows:

$$e^- = (1.86 \times 10^{-2}) \quad \frac{(1.96 \times 10^{-3})}{8.10} = 4.50 \times 10^{-6} \text{ M}$$

Table C.I

Determination of Electron Concentration from EPR Data

KNH_2	H	D	$I_e^* \times 10^3$	$e^- \times 10^6$
0.269	24.0	35.5	1.96	4.50
0.361	36.5	30.3	3.50	8.05
0.815	32.6	23.6	4.01	9.24
1.00	33.4	22.4	4.32	9.92
1.08	29.9	23.6	3.68	8.45
2.40	26.8	13.8	5.65	13.0

* $I_e = \frac{KHW^2}{MD}$

* W (width at half height) = 0.17

M (modulation amplitude) = 10

K = 1

APPENDIX D

Calculation of an Equilibrium Constant Using a Modified Debye-Hückel Theory

The equilibrium function describing the reaction:

$$e^-_{am} + NH_3 = NH_2^- + \frac{1}{2} H_2 \qquad (D\text{-}1)$$

can be written as

$$K = \frac{[NH_2^-]\ \gamma_{\pm 1}^2\ P_{H_2}^{1/2}}{[e^-]\ \gamma_{\pm 2}^{\ 2}} \qquad (D\text{-}2)$$

where $[NH_2^-]$ and $[e^-]$ represent the actual concentration of dissociated charged species and $\gamma_{\pm}$ the corresponding mean ionic activity coefficients. the activity coefficient of the hydrogen will be assumed to be unity. In the potassium amide solutions under study, we used relatively high concentrations of amide with respect to the electron and assumed that the ionic strength of the solution was due to the dissociation of the amide.

$$KNH_2 = K^+ + NH_2^- \qquad (D\text{-}3)$$

and the equilibrium for this reaction was written as

$$K_D = \frac{[K^+][NH_2^-]\ \gamma_{\pm}^{\ 2}}{[KNH_2]} \qquad (D\text{-}4)$$

where the activity of the neutral species was assumed to be unity and the ion concentrations are those of the dissociated species. Let α equal the degree of dissociation and C the stoichiometric concentration of KNH_2, then

$$K_D = \frac{C\,\alpha^2 \gamma_{\pm}^2}{1 - \alpha} \qquad \text{(D-5)}$$

The activity coefficient can be expressed by the Debye-Hückel approximation

$$- \ln \gamma_{\pm} = A(C\alpha)^{1/2}/(1 + B(C\alpha)^{1/2}) \qquad \text{(D-6)}$$

where

$$A = \frac{e^2}{2\ DkT}\left(\frac{8\pi\ Ne^2}{1000\ DkT}\right)^{1/2} \qquad \text{(D-7)}$$

and

$$B = \left(\frac{8\pi\ Ne^2}{1000\ DkT}\right)^{1/2} a \qquad \text{(D-8)}$$

In addition to reaction (D-3) we had to consider the reaction

$$M = M^+ + e^- \qquad \text{(D-9)}$$

where M represents the undissociated ion pair. The dissociation constant for this reaction is

$$K_o = \frac{[e^-][M^+]\gamma_{\pm}^2}{[M]} \qquad \text{(D-10)}$$

Gold and Jolly[10] have shown that both the electron and the undissociated ion pair have the same optical absorption spectrum. Therefore the total concentration of absorbing species is the sum of the electron and the undissociated ion pairs.

$$S = (e^-) + (M) \qquad \text{(D-11)}$$

By rearranging (D-10) we obtain an expression for [M]

$$(M) = \frac{(e^-)(M^+)}{K_D}\ \gamma_\pm^2 \qquad \text{(D-12)}$$

Substituting in Eq. (D-11) and rearranging we get

$$(e^-) = \frac{S}{1 + \frac{(M^+)\gamma_\pm^2}{K_D}} \qquad \text{(D-13)}$$

The values calculated for (e^-), $\gamma_\pm$ e^-, $[NH_2^-] = \alpha C$, and $\gamma_\pm$ KNH_2 were then substituted in Eq. (D-2) and the equilibrium constant determined. The results are shown in Table D-I.

The following calculation for the 1 M optical sample is given as an example. We assumed a value of 0.015 for the degree of dissociation α and calculated $C\alpha = 0.015$ and $(C\alpha)^{1/2} = 0.123$. Substituting in (D-6)

$$-\ln \gamma_\pm = \frac{11.75\ (0.123)}{1 + 1.29\ (0.123)} = 1.27$$

$$\gamma_\pm = 0.282 \qquad \gamma_\pm^2 = 0.0791$$

Substituting in (D-5) we calculated

$$K_D = (1)\ \frac{\alpha^2}{1-\alpha}\ (0.0791) = 2 \times 10^{-5}$$

$$\frac{\alpha^2}{1-\alpha} = 2.5 \times 10^{-4}$$

$$\alpha = 0.015$$

If the value had not agreed with the first approximation it would have been substituted back into Eq. (D-6) and the process repeated until the result converged to a constant value.

From the value calculated for α, we determined the ionic strength

$= C\alpha$. A value for B was calculated for the metal by assuming a value for $a = 4 \times 10^{-8}$ cm. An activity coefficient was calculated from (D-6)

$$- \ln \gamma_{\pm} = \frac{(11.75)(1.50 \times 10^{-2})^{1/2}}{1 + 2.83\ (1.50 \times 10^{-2})^{1/2}} = 1.065$$

$$\gamma_{\pm} = 0.344 \qquad \gamma_{\pm}^2 = 0.118$$

At 100 atmospheres of hydrogen pressure, the concentration of absorbing species was determined from $S = A/\epsilon d$ where the absorbance $A = 0.557$, the molar extinction coefficient $\epsilon = 1.1 \times 10^{+4}$ and the path length $d = 1.004$ (Table I), $S = 5.05 \times 10^{-5}$. Using a value of K_D for (D-9) $= 2 \times 10^{-2}$ we calculated the electron concentration by (D-13)

$$[e^-] = \frac{5.05 \times 10^{-5}}{1\ \ (1.5 \times 10^{-2})(0.344)^2/(2 \times 10^{-2})} = 4.63 \times 10^{-5}$$

Substituting these values into (D-2) we calculated on equilibrium constant

$$K_{eq} = \frac{(0.015)(0.282)^2(100)^{1/2}}{(4.63 \times 10^{-5})(0.344)^2} = 2.17 \times 10^5 .$$

TABLE D-I

Results of the Debye-Hückel Calculation

Conc of Amide	Degree of Dissociation	$\gamma_{\pm}(MMI_2)$	$\gamma_{\pm}(M)$	c^{-} $\times 10^{5}$	K $\times 10^{-5}$
2.0	1.95×10^{-2}	0.152	0.225	6.65	2.62
1.8	1.80	0.176	0.247	6.56	2.45
1.7	1.70	0.192	0.260	5.95	2.60
1.4	1.55	0.228	0.295	5.55	2.29
1.2	1.50	0.255	0.320	4.89	2.32
1.0	1.50	0.280	0.344	4.63	2.17
0.93	1.50	0.290	0.354	4.62	1.98
0.80	1.50	0.318	0.376	4.61	1.82
0.72	1.50	0.335	0.390	3.85	2.02
0.68	1.50	0.346	0.398	4.14	1.83
0.58	1.50	0.372	0.422	3.39	1.95
0.55	1.50	0.380	0.429	3.47	1.82
0.50	1.50	0.415	0.456	3.01	2.01
0.40	1.55	0.420	0.463	2.88	1.84
0.28	1.75	0.480	0.502	2.46	1.74
0.26	1.80	0.502	0.530	.250	1.65
0.20	1.90	0.511	0.540	2.41	1.40
0.19	1.90	0.516	0.545	2.22	1.48
0.16	1.98	0.538	0.555	2.62	1.14
0.15	2.05	0.539	0.563	1.63	1.71
0.067	2.70	0.620	0.635	1.47	1.15

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